

Oxidation of 2-Methyl-1-(1'-acetoxy-ethylidene)-cyclo- SOV/62-59-4-35/42
hexane by Osmium Tetroxide and Peracetic Acid

because so far no case has been known where continually rotating isomers were formed in a crystalline form (Refs 5 and 6). The compound (IV) was previously obtained (Ref 1) also by the reduction of cis-dioxycarboxylic acid (VI) with lithium aluminum hydride. Since with such a reduction of the carbalcoxy group the configuration is usually maintained the dioxycid (VI) should have "cis-treo" configuration. Cis-dioxycid (VII) and cis-triol (VIII) have cis-erythro configuration. Upon oxidation of acetate (II) with peracetic acid in chloroform a normal oxidation product is formed - the liquid acetate of glycidic alcohol (IX). A direct transition of hexanol (X) to cis-2-methyl-1-(ω -acetoxyacetyl)-cyclohexanol (X) could not be achieved by oxidizing hydroxylation by means of phenyliodosoacetate in the presence of osmium tetroxide (Ref 7). In the experiment the initial acetate was obtained unchanged. There are 9 references, 3 of which are Soviet.

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Oxidation of 2-Methyl-1-(1'-acetoxy-ethylidene)-cyclo- SOV/62-59-4-35/42
hexane by Osmium Tetroxide and Peracetic Acid

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii
nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy
of the Academy of Sciences, USSR)

SUBMITTED: August 8, 1958

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SOV/62-59-9-25/40

5(4)

AUTHORS:

Batuyev, M. I., Akhrem, A. A., Matveyeva, A. D.

TITLE:

Optical Investigation of Equatorial and Axial Carbonyl Groups of Some Substituted Cyclohexanes

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1665-1668 (USSR)

ABSTRACT:

The Raman spectra of the following compounds in the liquid phase, taken by means of the ISP-51 spectrograph and the E-612 Hilger spectrograph are investigated: Acetoxy-cyclohexane (I), acetyl-cyclohexane (II), 1-acetoxy-1-acetylcyclohexane (III), cis-2-methyl-1-acetoxy-1-acetylcyclohexane (IV), and trans-2-methyl-1-acetoxy-1-acetylcyclohexane (V). The physical data of the compounds are given in the table. The frequencies obtained are given in $\Delta\nu = \text{cm}^{-1}$. The configuration of the compounds (IV) and (V) was determined from the results of special analysis. Taking the largest substituent as basis, the conformation of (IV) was found to be trans-ee and trans-aa, that of (V) cis-ae and cis-ea.

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Optical Investigation of Equatorial and Axial Carbonyl Groups of Some Substituted Cyclohexanes SOV/62-59-9-25/40

The amounts of these isomers were found to be fairly equal in both cases, as was also the case for the two possible conformations of compound (III), of which equal amounts are formed. There are 4 tables and 2 Soviet references.

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR (Institute for Combustible Mineral Resources of the Academy of Sciences, USSR), Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: January 21, 1959

Card 2/2

5(3)

AUTHORS:

SOV/62-59-9-26/40

Batuyev, M. I., Akhrem, A. A., Kamernitskiy, A. V., Matveyeva, A. D.

TITLE:

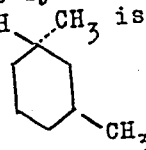
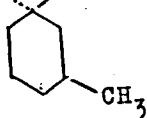
Optical Investigation of the Conformations of Cis and Trans-1,3-dimethylcyclohexanols

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 9, pp 1668-1670 (USSR)

ABSTRACT:

A reaction scheme for the synthesis of the substances investigated, (I) OH-CN and (II) OH-CH₃ is given from a previous paper.



The Auer-Skit transformation rule is valid for compounds (I) and (II) (Table). The Raman spectra of the compounds were taken in the liquid phase and in carbon tetrachloride solution. From the data obtained, the following conclusions were drawn: The alcohols form intermolecular hydrogen bonds in solution (bands split up into lines in the 3160-3530 cm⁻¹ range). These hydrogen bonds do not

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Optical Investigation of the Conformations of
Cis and Trans-1,3-dimethylcyclohexanols

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stem from the hydroxyl group. In the liquid phase complexes are formed by hydrogen bonding of the OH-group (continuous bands in the 3600 and 3614 cm^{-1} region). The hydroxyl groups generally have a similar position (equatorial) in the associated complex. Thus, in (I) their position is cis-1a3a and in (II) trans-1a3e. Their position was determined at cis-1e3e in (I) and trans-1a3e and trans-1e3a in (II) (equatorial and equatorial-axial), relative to the CH_3 -group outside the hydrogen bond as the largest substituent. If one disregards the nomenclature of these configurations and conformations by reason of their formation, and regards solely their real structure, deduced from their physical properties, as well as taking into account the transformation rule by Barton and Hassel (the configuration is determined by the position of the largest substituent) one would have to redefine the cis-1a3a conformation of (I), the form predominant in associated molecules, of (I), and also the

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Optical Investigation of the Conformations of
Cis and Trans-1,3-dimethylcyclohexanols ..

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trans-1a3e conformation of (II). The nomenclature of these conformations would then be trans-1e3a and cis-1e3a respectively. There are 1 table and 3 Soviet references.

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR
(Institute for Combustible Mineral Resources of the Academy of Sciences, USSR), Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences, USSR)

SUBMITTED: January 21, 1959

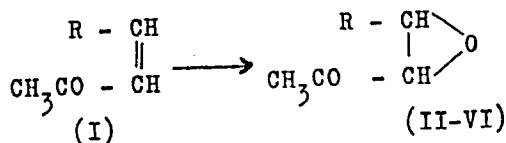
Card 3/3

AKHREM, A.A.; TITOV, Yu.A.

Chemistry of 19-norsteroids. Usp.khim. 33 no.2:151-181 F '64.

1. Institut organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.
(MIRA 17:10)

5 (3)
 AUTHORS: Tishchenko, I. G., Akhrem, A. A., Nazarov, I. N. (Deceased) SOV/79-29-3-14/61
 TITLE: α -Keto Oxides (α -Ketookisi). IX. Oxides of Alkylidene Acetones and Some Other α,β -Unsaturated Ketones (IX. Okisi alkili-denatsetonov i nekotorykh drugikh α,β -nepredel'nykh ketonov)
 PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 809-820 (USSR)
 ABSTRACT: The authors carried on their earlier investigations (Refs 1-3, 5) and investigated the oxidation with alkaline hydrogen peroxide of the following compounds: ethylidene acetone (penten-2-one-4) propylidene acetone (hexen-3-one-2), trans-n-butylidene acetone (hepten-3-one-2), trans-isobutylidene acetone (5-methylhexen-3-one-2), as well as 3-methylhepten-3-one-2,1-methoxy-5-methylocten-4-one-3 and 5-methyloctadiene-1,4-one-3. It was established that in the action of alkaline hydrogen peroxide upon the alkylidene acetones (I) in methanol solution, the corresponding α -keto oxides (II-VI) form in cooling:



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α -Keto Oxides. IX. Oxides of Alkylidene Acetones and Some Other α,β -Unsaturated Ketones

where in (II) $R=CH_3$ (V) $R=iso-C_3H_7$
" (III) $R=C_2H_5$ (VI) $R=iso-C_4H_9$
" (IV) $R=n-C_3H_7$.

In the same way, compound (VIII) (Scheme 2) resulted from (VII) and compounds (XI) and (XII) (Scheme 3) from (IX) and (X). It was shown that under the influence of diluted sulphuric acid solutions, the alkylidene acetones and the oxide of 3-methylhepten-3-one-2 isomerize into the α -diketones and also hydrolyze into the corresponding keto glycols. The ultraviolet absorption spectra of the oxides of ethylidene-, propylidene-, trans-n- and trans-isobutylidene-, isovalerylidene acetone and of 3-methylhepten-3-one-2 were recorded. All these acetones have one and the same absorption band at 285-290 m μ , which refers to the carbonyl group (Figs 1-2). There are 2 figures and 27 references, 12 of which are Soviet.

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SOV/79-29-3-14/61

α -Keto Oxides. IX. Oxides of Alkylidene Acetones and Some Other α,β -Unsaturated Ketones

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR i Belorusskiy gosudarstvennyy universitet
(Institute of Organic Chemistry of the Academy of Sciences, USSR and Belorussian State University)

SUBMITTED: January 3, 1958

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5.3100

5(3)

67914

SOV/20-129-5-21/64

AUTHORS: Batuyev, M. I., Akhrem, A. A., Matveyeva, A. D.

TITLE: Optical Investigation of the Conformations of Acetyl Cyclohexene and Its Oxide

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 5,
pp 1038 - 1041 (USSR)

ABSTRACT: Table 1 shows the physical properties of acetyl cyclohexene and its oxide which was produced by the aid of alkaline hydrogen peroxide (Ref 1, see Scheme). The Raman spectra of both these substances were taken by means of the Soviet 3 prism spectrograph ISP-51 with a central chamber and the Hilger spectrograph Ye612 in the liquid phase. The exciting frequency 4358 Å stemmed from a mercury lamp. The measured frequencies are specified. The presence of frequencies in the region of the triple bond (2096, 2111 cm^{-1}) in the spectra of both substances points to the fact that they still contained residues of the ethynyl compound utilized for their synthesis. i - C frequencies showed that the oxidation of acetyl cyclohexene was incomplete and that the oxidation product is a mixture from acetyl cyclohexene and its oxide. The oxide, how-

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Optical Investigation of the Conformations of Acetyl SOV/20-129-5-21/64
Cyclohexene and Its Oxide

ever, is clearly predominant. It was electronographically confirmed (Refs 2,3) that the carbon atoms of the double bond C_1 and C_2 are placed on or approximately on the same plane. The molecule exhibits half-chair-shaped (polukreslovidnyy) conformations (Ref 4) (see Scheme). The valencies are quasi-equatorial (e') and quasi-axial (a') at the atoms C_3 and C_6 , whereas they are equatorial (e) and axial (a) at C_4 and C_5 . Since the half-chair-shaped confirmation of cyclohexene is energetically by 2.7 kcal/mol more advantageous, and since the rules established by Barton and Khassell' (Ref 7) are evidently still valid for substituted cyclohexenes, the half-chair-shaped confirmation in acetyl cyclohexene is apparently predominant. In this connection, the acetyl group is placed on the plane of atoms $C_1C_2C_3C_6$ or on an approximated plane (see Scheme). There are no reasons for denying the conservation of the acetyl group position in the case of conversion $(I) \rightleftharpoons (II)$. The carbonyl group frequency is divided into 1663 and 1672 cm^{-1} . The ethylene bond frequency is practically not divided into a doublet. The authors are inclined to assume that


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the division of the carbonyl frequency is to be explained by the possible double position of carbonyl with respect to the ethylene formation C=C of the ring, namely, the cis-oid position ((I) \rightleftharpoons (II)) and the trans-oid position ((III) \rightleftharpoons (IV)) (see Scheme). The oscillation frequency of the ethylene bond remains practically unchanged. The oxidation of the acetyl cyclohexene on the double bond leads to the formation of a 3-membered oxide ring

 C—C, whose C-C-bond belongs to the 6-membered carbon ring. The half-chair-shaped conformation of the 6-membered ring is conserved in the acetyl cyclohexene oxide (Ref 9). If the above-mentioned position of the acetyl group is conserved, the oxygen atom of the 3-membered ring (see above) is placed on a plane which is perpendicular to the plane C₁C₂C₃C₆. The above concepts were concretized by optical data supplied by the authors. It was finally confirmed that acetyl cyclohexene oxide exists in cis-oid (V) \rightleftharpoons (VI) and trans-oid (VII) \rightleftharpoons (VIII) conformations. The causes leading to the formation of both these forms are

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Optical Investigation of the Conformations of Acetyl
Cyclohexene and Its Oxide

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SOV/20-129-5-21/64

different in acetyl cyclohexene and in its oxide. There are 1
table and 9 references, 3 of which are Soviet. ✓

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR (Institute
of Mineral Fuels of the Academy of Sciences, USSR)

PRESENTED: July 15, 1959, by B. A. Arbuzov, Academician

SUBMITTED: July 3, 1959

Card 4/4

AKHREM, A.A.

PAGE 1 BOOK EXAMINATION 507/1983

Lantrop, Olevskiy
 Topov, G. G. Stereocyclic organoborates especially (Problems in the Theory of
 the Structure of Organic Compounds) [Lantrop] 1960. 239 p. Kireva 21p
 inserted. 3,725 copies printed.

Sponoring Agency: Lantrop'syriyevskaya Lantrop'syriyevskaya universitet in
 A.A. Zhukovskiy.

Boop, M. I. 74. Fomichyev; M. I. V. D. Plavny; Tech. M. I. 3. D. Vokhlagina.
 PROPOS: This collection of articles is intended for chemists and organic
 chemists.

COPYRIGHT: The collection is concerned with the scientific legacy of A. I. Fomichyev,
 and includes the results of his theoretical views and the application in com-
 position with the development of theoretical organic chemistry. The articles re-
 view the development of the structure, reactivity and optical properties of various classes
 of organic compounds: substituted acetylene and optical isomers, saturated
 and unsaturated alcohols, glycols and organic compounds. No personal titles
 are mentioned. References accompany each article.

Domini, R. I., R. I. Kollinsky, and V. A. Chelkova. Development of A. I. Fomichyev's
 research in the field of polymeric organic compounds. 64

Lobachev, A. I. Development of A. I. Fomichyev's ideas on the synthesis of
 terpenes and related compounds by the Soviet School of Chemistry 126

Terpenes and Related Compounds by the Soviet School of Chemistry 135

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Terpenes and Related Compounds by the Soviet School of Chemistry 224

Terpenes and Related Compounds by the Soviet School of Chemistry 224

ADDITIONAL: Library of Congress (20176-144)

BATUYEV, M.I.; AKHREM, A.A.; MATVEYEVA, A.D.

Optical study of some acetylenic alcohols and their acetates.
Izv. AN SSSR.Otd. khim. nauk no.12:2201-2207 D '60. (MIRA 13:12)

1. Institut goryuchikh iskopayemykh AN SSSR i Institut organicheskoy khimii im.N.Z.Zelinskogo AN SSSR.
(Acetylene compounds--Optical properties)

BATUYEV, M.I.; AKHREM, A.A.; KAMERNITSKIY, A.V.; MATVEYEVA, A.D.

Optical study of the conformations of cyclohexanone and some of
its derivatives. Dokl.AN SSSR 133 no.5:1077-1080 Ag '60.
(MIRA 13:8)

1. Institut goryuchikh iskopayemykh Akademii nauk SSSR i Institut
organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR.
(Cyclohexanone)

MASHER, Dzh. [Musher, J.I.]; AKHREM, A.A.

Nuclear magnetic resonance study of the configuration of saturated cyclic systems. 2-Methyl-1-hydroxycyclohexylethylene oxides and some 1-hydroxydecalylethylene oxides. Dokl.AN SSSR 134 no.2: 354-357 S '60. (MIRA 13:9)

1. Fizicheskaya laboratoriya Garvardskogo universiteta, SShA
i Institut organicheskoy khimii im. N.D.Zelinskogo Akademii nauk
SSSR. Predstavleno akad. B.A.Kazanskim. (Nuclear magnetic resonance)
(Ethylene oxide)

BATUYEV, M.I.; AKHREM, A.A.; KAMERNITSKIY, A.V.; MATVEYEVA, A.D.

Optical study of conformations of cyclopentanone and α -chloro-
cyclopentanone. Izv.AN SSSR.Otd.khim.nauk no.6:1138-1141 Je '61.
(MIRA 14:6)

1. Institut goryuchikh iskopayemykh AN SSSR i Institut organicheskoy
khimii im. N.D.Zelinskogo AN SSSR.
(Cyclopentanone) (Isomers)

BATUYEV, M.I.; AKHREM, A.A.; KAMERNITSKIY, A.V.; MATVEYEVA, A.D.

Optical investigation of conformations of cyanohydrins of
some derivatives of cyclohexanone. Izv.AN SSSR.Otd.khim.nauk
no.10:1813-1816 O '61. (MIRA 14:10)

1. Institut goryuchikh iskopayemykh AN SSSR i Institut organicheskoy
khimii im. N.D.Zelinskogo AN SSSR.
(Cyanohydrins) (Cyclohexanone)

AKHREN, A.A.

KAMNEVICH, A.A.; AKHREN, A.A.

Summary: Study of reactions of nucleophilic addition to the carbonyl group of cyclic ketones. Usp. Khim. 30 no.2:145-183 7 '61.
(NIPA 14:2)

1. Institut organicheskoy khimii im.N.D.Zelinskogo AN SSSR.
(Addition reactions) (Carbonyl group)
(Ketones)

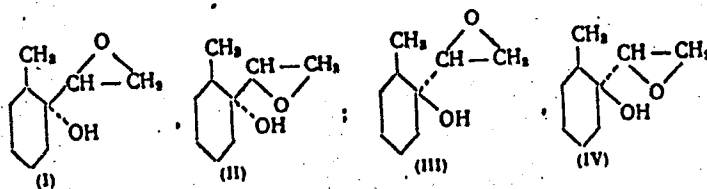
S/020/61/137/005/017/026
B103/B208

AUTHORS: Batuyev, M.I., Akhrem, A.A., and Matveyeva, A.D.

TITLE: Optical study of the conformations of 2-methyl-1-hydroxy-
-cyclohexyl-ethylene oxides

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 5, 1961, 1113 - 1116

TEXT: It is the purpose of the present study to define the structure of
the following glycidic alcohols:



which had been obtained by oxidation by peracetic acid in chloroform from

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cis-2-methyl-1-vinyl cyclohexanol: (I) and (II); and trans-2-methyl-1-vinyl-cyclohexanol: (III) and (IV); and which were assumed to have the above structural formulas. All four alcohols have different melting points. Their structures were studied by their Raman spectra recorded on the USSR spectrograph of the type MCH-51 (ISP-51), and on an E612 Hilger spectrograph. It is concluded from the data (Table 1) that a hydrogen bond exists between the hydroxyl group of these alcohols in liquid state and the oxygen atom of the oxide ring. This is confirmed by the fact that the O - H frequency is a blurred narrow band which is quite different in the two trans-isomers. It is narrow ($\sim 45 \text{ cm}^{-1}$) in the low-melting isomer (IV) ($40.5 - 41^\circ\text{C}$), and broader ($\sim 200 \text{ cm}^{-1}$) in the high-melting isomer (III) ($75 - 75.5^\circ\text{C}$). This is assumed to indicate a predominance of the intramolecular H-bond in (IV), whereas in (III) the intermolecular bond prevails. This difference seems to exert a considerable effect on the melting points. This fact was used for the identification of (III) and (IV). If the different melting-points of (I) and (II) have the same reason, the higher-melting alcohol (I) ($43 - 43.5^\circ\text{C}$) is that with intermolecular H-bond,

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while the liquid (II) has the intramolecular bond. This assumption was confirmed optically. In a considerable part of the molecules of (II) in the liquid phase the O-H group is released from the intramolecular H-bond and enters the intermolecular H-bond. The threo-isomer is thus partly converted to the erythro-isomer, or to an isomer having a similar position of the oxide ring as the erythro-isomer. The conversion of the erythro-isomer to the threo-isomer can hardly be confirmed optically in the case of (I). The authors conclude from these facts that the two types of H-bond represent the most important stabilizing factors in the case of erythro-threo-isomerism. The energy of the H-bond is not high (~ 3 kcal/mole). These bonds therefore cause a considerable difference of the mentioned isomerism in crystalline state, but not in liquid or super-cooled-liquid state. The intramolecular bonds are, as a rule, not destroyed in 20% solutions of these alcohols in CCl_4 , which was also optically confirmed. The complexes of (I) and (III) with several members, which are associated by the intramolecular H-bond, are destroyed, while dimeric complexes are preserved, and monomers are formed. The authors conclude from the optical data that under their experimental con-

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ditions each of the four alcohols mentioned exists in two conformations. The prevalent conformation are: in (I) - cis-ea (Fig. 1), in (III) and (IV) - trans-ee; in (II) both conformations appear to about the same extent. There are 1 figure and 6 Soviet-bloc references.

ASSOCIATION: Institut goryuchikh iskopayemykh Akademii nauk SSSR
(Institute of Mineral Fuels of the Academy of Sciences USSR)
Institut organicheskoy khimii im. N. D. Zelinskogo
Akademii nauk SSSR (Institute of Organic Chemistry imeni
N. D. Zelinskiy of the Academy of Sciences USSR)

PRESENTED: November 28, 1960, by B. A. Arbuzov, Academician

SUBMITTED: December 29, 1960

Card 4/74

AKHREM, A.A.; KUZNETSOVA, A.I.; TITOV, Yu.A.; LEVINA, I.S.

Separation of acetylenic alcohols and glycols by means of thin layer chromatography on aluminum oxide. Izv.AN SSSR Otd.khim.-nauk no.4:657-661 Ap '62. (MIRA 15:4)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Alcohols) (Chromatographic analysis)

S/062/63/000/001/009/025
B101/B186

AUTHORS:

Bystrov, V. F., Pozdnyakova, T. Ye., Yelizarova, A. N.,
and Akhrem, A. A.

TITLE:

Structural analysis of chemical compounds based on their
nuclear magnetic resonance spectra. Communication 2.
Determination of the structure and conformation of some
substituted cyclopentenones

PERIODICAL:

Akademiya nauk SSSR. Izvestiya. Otdeleniye
khimicheskikh nauk, no. 1, 1963, 66-74

TEXT: The synthesis of the erythro isomer IA and threo isomer IB of 3,5-dimethyl-5-(α -acetoxyethyl)- Δ^2 -cyclopentenone by condensation of 3,5-dimethyl- Δ^2 -cyclopentenone with vinyl acetate has already been described (Izv. AN SSSR, Otd. khim. n., in press). That reaction also produced the erythro and threo isomer of 3,5-dimethyl-5-(α -acetoxyethyl)- Δ^3 -cyclopentenone (IIA, IIB) and the 2-ethylidene-3,5-dimethyl- Δ^4 -cyclopentenone (III). By analyzing the high resolution proton magnetic resonance (p.m.r.) spectra it was possible to define the structure and conformation of IA,

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Structural analysis of chemical ...

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IB and III as well as of 3,5-dimethyl- Δ^2 -cyclopentenone (IV), 3,5-dimethyl- Δ^4 -cyclopentenone (V), 3,5-dimethyl-5-vinyl- Δ^2 -cyclopentenone (VI), 3,5-dimethyl-5-(α -acetoxyethyl)-cyclopentanone (VIIA, VIIB), 3,5-dimethyl-5-(α -hydroxyethyl)- Δ^2 -cyclopentenone (VIII A, VIII B), and 3,5-dimethyl-5-(α -hydroxyethyl)-cyclopentanone (IXA) which were synthesized for comparison. The p.m.r. spectra of 0.2-0.5 M solutions in CCl_4 were taken at room temperature and at 20.529 Mc. Hexamethyl disiloxane was used as internal standard. The spectra were analyzed according to J. T. Arnold and M. E. Packard (J. Chem. Phys., 19, 1608 (1951)). The slight difference between the spectra of IA and IB led to the conclusion that there is no structural difference but only a different steric orientation of the groups; this was confirmed by converting IA and IB into VI. Equally, IXA was obtained by hydrogenation from VIIIA as well as from VIIIB. Conclusions: The isomerism is based on a different position of the substituents at the asymmetric C_6 atom. Two steric series are possible with 3 conformations each (Fig. 6). One of these conformations must outnumber the two other. The IR spectra of VIIIA, VIIIB and IXA showed that an intramolecular H bond exists at the hydroxy group of VIIIA and IXA, which is absent in VIIIB.

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Hence, the compounds IA, VIIA, VIIIA and IXA have the structure a with predominant conformation 3a, the isomer compounds IB, VIIB and VIIIB have the structure b with predominant conformation 3b. The structure of III was confirmed by the p.m.r. spectrum. The p.m.r. spectra of IIA and IIB were not taken, since these isomers could not be separated. There are 7 figures and 1 table.

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR);
Institut organicheskoy khimii Akademii nauk SSSR
(Institute of Organic Chemistry of the Academy of Sciences USSR)

SUBMITTED:

June 18, 1962

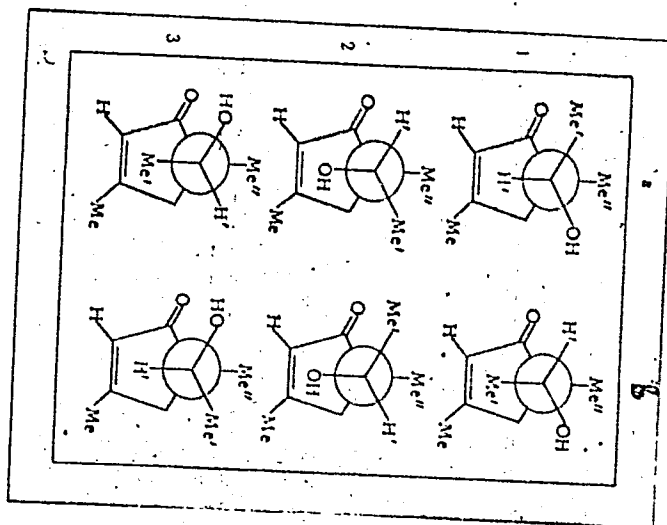
Fig. 6. Conformations of the rotation isomers of 3,4-dimethyl-(α -hydroxy-ethyl)- Δ^2 -cyclopentenone (VIIIA and VIIIB).

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Structural analysis of chemical ...

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Fig. 6



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S/062/63/000/001/015/025
B101/B186

AUTHORS: Yelizarova, A. N., Pozdnyakova, T. Ye., and Akhrem, A. A.

TITLE: Chemistry of cyclopentenones. Communication 6. Conversions of erythro- and threo-isomers of 3,5-dimethyl-5-(α -acetoxyethyl)-cyclopentenones

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 1, 1963, 129 - 136

TEXT: To clarify the configuration of erythro-3,5-dimethyl-5-(α -acetoxyethyl)- Δ^2 -cyclopentenone (IA), m.p. 69-70°C, and its threo-isomer (IB), m.p. 51-52°C, and of the analogous compounds (IIA, IIB) of Δ^3 -cyclopentenone, the following reactions were carried out: Hydrolysis of IA and IB in 10% HCl at 100°C yielded the corresponding 3,5-dimethyl-5-(α -hydroxyethyl)- Δ^2 -cyclopentenones IIIA (yield 83%, b.p. 92-93°C/5mm-Hg, crystallizes when standing, m.p. 40-41°C) and IIIB (yield 87%, m.p. 72-73°C); IB hydrolyzed more readily than IA. Hydrolysis of IIA, IIB yielded the corresponding α -hydroxyethyl derivatives IVA, IVB. IA and IB did not hydrolyze in 20%

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NaOH at 100°C; only small amounts of IIA, IIB were obtained in 40% NaOH; the initial 3,5-dimethyl- Δ^2 -cyclopentenone formed in 60% yield. Hydrogenation of IA or IIA with platinum catalyst yielded 3,5-dimethyl-5-(α -acetoxyethyl)-cyclopentanone (VIA), m.p. 41°C; likewise, the corresponding epimer VIB was formed from IB or IIB, yield 73%, b.p. 84-85°C/4 mm Hg, n_D^{20} 1.4446, d_4^{20} 1.0060. Hydrogenation of IIIA, IIIB, IVA, and IVB only yielded 3,5-dimethyl-5-(α -hydroxyethyl)-cyclopentanone (VA), yield 81%, b.p. 88-90°C/6 mm Hg, n_D^{20} 1.4604, d_4^{20} 0.9860, which was formed also by acidolysis of VIA, this indicating epimerization of the threo-ketone alcohol IIIB. In oxidation of IIIA and IIIB with CrO_3 and acetic acid, one of the two centers of asymmetry disappears and only 3,5-dimethyl-5-acetyl- Δ^2 -cyclopentanone (VII) is formed, yield 80%, b.p. 92-93°C/5 mm Hg, n_D^{20} 1.4877, d_4^{20} 1.0471. Such isomerization also occurs in the formation of 2,4-dinitrophenyl hydrazone (2,4-DNPH) of IB and IIIB. Both IA and IIIA, and IB and IIIB, form the same 2,4-DNPH, m.p. 158°C, which, saponified with HCl in acetone, gives

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IIIA. Likewise, VIB and VA form only one type of 2,4-DNPH, m.p. 147.5°C, which forms VA by saponification. An isomerization similar to the reaction described by B. Ellis (Mrs.) et al. (J. Chem. Soc., 1961, 4111) is assumed for the asymmetric C₆. The higher stability of IA, as compared with IB, indicates that the compounds of the A series have erythro-, and the compounds of the B series threo-configuration. Reduction of VIA with LiAlH₄ in ether yielded a chromatographically separable mixture of the two epimers of 3,5-dimethyl-5-(α-hydroxyethyl)-cyclopentan-1-ol, yield 90%, b.p. 107-109°C/4 mm Hg, n_D²⁰ 1.4708, d₄²⁰ 0.9946, which was not further investigated. There are 3 figures.

ASSOCIATION: Institut organicheskoy khimii im. N. D. Zelinskogo Akademii nauk SSSR (Institute of Organic Chemistry imeni N. D. Zelinskiy of the Academy of Sciences USSR)

SUBMITTED: June 18, 1962

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SOV/79-29-3-3/61

5(3)
AUTHORS: Nazarov, I. N. (Deceased), Burmistrova, M. S., Akhrem, A. A.

TITLE: Synthesis of the Simplest Analogues of Corticosteroids (Sintez prosteyshikh analogov kortikosteroidov). VII. Introduction of the Dioxycetone Side Chain by Hydration of Acetylene Alcohols (VII. Vvedeniye dioksiatsetonovoy bokovoy tsepi metodom gidratatsii atsetilenovykh spirtov)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 3, pp 735-744 (USSR)

ABSTRACT: The authors earlier described (Ref 1) the bromohydrin-, di-bromoketol- and glycide method of introducing the oxidized side chains into the cyclic compounds. They were likewise interested in the introduction of the dioxycetone side chain, which is characteristic of some hormones, by the hydration of acetylene alcohols. Although after the completion of their investigations some reports appeared on the synthesis of the simplest cortisone analogues, in which the same method of introducing the above chain had been applied, their investigation results still had to be published, inasmuch as the yields of the initial products obtained in the latter investigations were higher, than had been those published according to references 2-4. At first the dimethyl ethynyl carbinol (I),

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Synthesis of the Simplest Analogues of Corticosteroids. VII. Introduction of the Dioxycetone Side Chain by the Hydration Method of Acetylene Alcohols

which was obtained according to Favorskiy's reaction by condensation of the acetylene with acetone (Ref 5), was used as an initial product. In the hydration of carbinol (I) in the presence of sulphuric mercury, the dimethyl acetyl carbinol (II) (Ref 6), which is transformed into bromo acetyl dimethyl carbinol (III) by dioxane bromide, results in a high yield. In the action exerted upon this by alcoholic caustic potash lye, dimethyloxyacetyl carbinol (IV) (Scheme 1) is formed. On the reaction of the acetate of dimethyl acetyl carbinol (V) (Ref 6) with dioxane dibromide, compound (VI) is formed, which in the action of alkaline caustic potash lye likewise passes over to (IV) and in acetolysis forms diacetate of (IV) = (VII) by the aid of potassium acetate in methanol. Also the following compounds were used as further initial products for this reaction: 1-ethynylcyclohexanol (VIII); 3,5-dimethyl-1-ethynylcyclopentanol (XV); cis-2-methyl-1-ethynylcyclohexanol (XX) and 3,8-dimethyl-1-ethynyl- Δ^5 -tetrahydroindanol (XXVII). Their hydration with subsequent bromination and saponification of the forming α -bromo ketols led to compounds, which likewise contain the dioxycetone

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Synthesis of the Simplest Analogues of Corticosteroids. VII. Introduction
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side chain. There are 10 references, 7 of which are Soviet.

ASSOCIATION: Institut organicheskoy khimii Akademii nauk SSSR
(Institute of Organic Chemistry of the Academy of Sciences,
USSR)

SUBMITTED: January 3, 1958

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AKHREM, Afanasiy Andreyevich for Doc Chem Sci on the basis of dissertation defended
9 June 59 in Council of Inst of Organic Chem im Zelinskiy, Acad Sci USSR, entitled
"Study in the field of ^{the} synthesis and stereochemistry of analogues of cortico-
steroids. Methods of building and the stereochemistry of a corticoid side chain ."
(BMVISO USSR, 1-61, 25)

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AKHREM, A.A.; GERZHNAMER, S. [Hermanek, S.]; SYGORA, K. [Syhora, K.]

New case of the closure of the 5 α , 6 α -oxide ring in the androstane series.. Izv. AN SSSR Otd. khim. nauk no.10:1898-1899 O '60.
(MIRA 13:10)

1. Institut organicheskoy khimii im. N.D. Zelinskogo Akademii nauk SSSR i Nauchno-issledovatel'skiy institut prirodnykh lekarstvennykh veshchestv, Praga.

(Androstane)

(Cyclization)

5.3400,5.3900

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SOV/79-30-3-8/69

AUTHORS: Kamernitskiy, A. V., Akhrem, A. A.

TITLE: The Simplest Analogs of Corticosteroids. IX.
Stereochemistry of Nucleophilic Addition to the
Carbonyl Group. 6. Steric Course of Cyanohydrin
and Metallo-Organic Synthesis Based on 3-Methylcyclo-
hexanone

PERIODICAL: Zhurnal obshchey khimii, 1960, Vol 30, Nr 3,
pp 754-764 (USSR)

ABSTRACT: It was established previously (this journal, 1958,
Vol 28, p 1458; 1955, Vol 25, p 1345) that 2-methyl-
cyclohexanone (I) in reaction with acetone cyanohydrin
yields a mixture of cyanohydrins consisting of 75-80%
cis forms, and 25-20% trans forms, and that the acetylene
synthesis with (I) under pressure gives a mixture of
60% cis and 40% trans isomers, whereas (I) in reaction
with methylmagnesium iodide gives 25% cis and 75% trans
forms. The preliminary investigation of the above
reactions in application to 3-methylcyclohexanone
(Izv. AN SSSR, 1959, p 748, abstract 71916) showed

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that the steric course of these reactions is analogous to that observed for 2-methylcyclohexanone. In the present study, 3-methylcyclohexanone in reaction with acetone cyanohydrin gave a mixture of 1-cyano-3-methylcyclohexanols consisting of 25% cis and 75% trans forms; the reaction with methylmagnesium iodide yielded a mixture of 1,3-dimethylcyclohexanols consisting of 60% cis and 40% trans forms. These and other reactions of 3-methylcyclohexanone and its derivatives confirmed the formerly advanced theory that cyanohydrin and acetylene synthesis with 3-methylcyclohexanone leads to a predominance of ae-conformation, and the metallo-organic synthesis, to the predominance of ee-conformation. In the first instance, the cis form is obtained owing to the predominance of the introduction of axial H, CN, or $C \equiv CH$ substituents; in the second instance, the introduction of equatorial CH_3 substituent leads to the predominance of the trans form. It was suggested that the introduction of the substituents in the axial position is determined by the polar orientation of the nucleophilic reagent which depends on the mechanism

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of the ionic reaction of the nucleophilic addition; the introduction in the equatorial position depends on the steric hindrances due to the axial meta-substituents (including also the hydrogen atoms). There are 2 tables; and 29 references, 7 U.S., 4 U.K., 3 French, 1 Belgian, 2 Swiss, 2 German, 10 Soviet. The 5 most recent U.S. and U.K. references are: D. S. Noyce, D. B. Denney, J. Am. Chem. Soc., 72, 5743 (1959); D. H. Barton, R. Cookson, Quart. Revs., 10, 44 (1956); E. L. Eliel, R. G. Haber, J. Org. Chem., 23, 2041 (1958); R. O. Clinton, R. G. Christiansen, H. C. Neumann, S. C. Laskowski, J. Am. Chem. Soc., 80, 3389 (1958); G. F. Hennion, F. X. O'Shea, *ibid.*, 80, 614 (1958).

ASSOCIATION:

Institute of Organic Chemistry, Academy of Sciences
USSR (Institut organicheskoy khimii Akademii nauk
SSSR)

SUBMITTED:

May 14, 1959

Card 3/3

AKHREM, A.A.; TITOV, Yu.A.; MINAYEVA, I.N.

Synthesis of methyl ether of 18-nor-D-homoequilinenin. Izv. AN SSSR.
Otd.khim.nauk no.6:1164 Je '61. (MIRA 14:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Estrapentaenone)

AKHREM, A.A.; KUZNETSOVA, A.I.

Use of thin lamination chromatography for the separation of steroid compounds. Med. prom. 15 no.2:57-62 F '61. (MIRA 14:3)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.
(CHROMATOGRAPHY) (STERIODS)

AKHREM, A.A.; KUZNETSOVA, A.I.

Using thin-layer chromatography for the separation of steroid compounds. Dokl. AN SSSR 138 no.3:591-594 My '61. (MIRA 14:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR. Predstavleno akademikom B.A.Kazanskim.
(Chromatographic analysis) (Steroids)

AKHREM, A.A.; UKHOVA, L.I.; USKOVA, N.F.

Heterocyclic analogs of corticosteroids. Report No.1:
Syntheses based on 1,2-dimethyl-4-oxo-decahydroquinoline.
Izv. AN SSSR Otd.khim.nauk no.2:304-309 F '62.

(MIRA 15:2)

1. Institut fiziko-organicheskoy khimii AN Belorusskoy SSR
i Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Quinoline)
(Corticosteroids)

AKHREM, A.A.

Analogs of corticosteroids. Report No.11: 1-Acetylcyclohexene oxide
and its conversions. Izv. AN SSSR. Otd.khim,nauk no.5:845-850
My '62. (MIRA 15:6)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Corticosteroids) (Ketone)

AKHREM, A.A.; KAMERNITSKIY, A.V.; PAVLOVA-GRISHINA, N.S.

Stereochemistry of the reactions of nucleophilic addition to the carbonyl group of cyclic ketones. Report No.5: Stereochemistry of cyanohydrin synthesis with 2-chlorocyclohexanone. Izv.AN SSSR.Otd.khim.nauk no.6:1050-1056 '62. (MIRA 15:8)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Cyanohydrins) (Cyclohexanone)

AKHREM, A.A.; ZAVEL'SKAYA, I.G.

Transformed steroids. Part 1: New reaction in the series 5 α -oxy,
6 β -acetoxy derivatives of androstane. Zhur. ob. khim. 32 no.1:
50-58 Ja '62. (MIRA 15:2)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.
(Androstane)

YELIZAROVA, A. N.; POZDNYAKOVA, T. Ye.; AKHREM, A. A.

Chemistry of cyclopentenone. Report No. 4: Condensation of
3,5-dimethyl- Δ^2 - and Δ^4 -cyclopentenones with vinyl acetate.
Izv. AN SSSR Otd. khim. nauk no.12:2167-2175 D '62.
(MIRA 16:1)

1. Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR.

(Cyclopentenone) (Vinyl acetate)

YELIZAROVA, A. N.; POZONYAKOVA, T. Ye.; AKHREY, A. A.

Chemistry of cyclopentenones. Report No. 5: Condensation of 3,5-dimethyl- Δ^2 - and 3,5-dimethyl- Δ^4 -cyclopentenones with vinyl acetate in the presence of catalysts. Izv. AN SSSR Otd. khim. nauk no.12:2175-2182 D '62. (MIRA 16:1)

1. Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR.

(Cyclopentenone) (Vinyl acetate)

BYSTROV, V. F.; POZDNYAKOVA, T. Ye.; YELIZAROVA, A. N.; AKHREM, A. A.

Study of the structure of chemical compounds by nuclear magnetic resonance spectra. Report No. 2: Determination of the structure and conformation of some substituted cyclopentenones. Izv. AN SSSR. Otd. khim. nauk no.1:66-74 '63. (MIRA 16:1)

1. Institut khimicheskoy fiziki AN SSSR i Institut organicheskoy khimii AN SSSR.

(Cyclopentenone--Spectra) (Chemical structure)

AKHREM, A. A.; RESHETOVA, I. G.

Transformed steroids. Report No. 2: Synthesis and stereochemistry of C6- and C21-fluorinated steroids. Izv. AN SSSR. otd. khim. nauk no.1:115-124 '63. (MIRA 16:1)

1. Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR.

(Steroids) (Stereochemistry)

AKHREM, A.A.; LEVIN, I.S.; TITOV, Yu.A.

Condensation of 3-(4-methoxyphenyl)-2-cyclohexen-1-one with maleic anhydride. Izv. AN SSSR. Otd. khim. nauk no. 10: 1891-1893 0 '62. (MIRA 15:10)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.
(Cyclohexenone) (Maleic anhydride)

AKHREM, A.A.; USTYNYUK, T.K.

Rearrangement of 21,21-dibromo- Δ^4 -pregnen-17 β -ol-3, 20-dione
acetate to isomeric Δ^4 -pregnene-17 β -20 α -diol-21-oic acids. Izv.
AN SSSR. Otd.khim. nauk no.4:768 Ap '63. (MIRA 16:3)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Pregnenedione) (Pregnenic acid)

YELIZAROVA, A. N.; POZDNYAKOVA, T. Ye.; AKHREM, A. A.

Chemistry of cyclopentenones. Report No. 6: Conversions of erythro- and threoisomers of 3,5-dimethyl-5- (α -acetoxyethyl)-cyclopentenones. Izv. AN SSSR. Otd. khim. nauk no.1: 129-136 '63. (MIRA 16:1)

1. Institut organicheskoy khimii im. N. D. Zelinskogo AN SSSR.
(Cyclopentenone) (Isomerization)

AKHREM, A.A.; UKHOVA, L.I.; SAKOVICH, N.F.

Synthesis and stereoisomerism of N-oxides of the decahydroquinoline series. Izv.AN SSSR Otd.khim.nauk no.5:838-844 My '63.
(MIRA 16:8)

1. Institut fiziko-organicheskoy khimii AN BSSR i Institut
organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Quinoline) (Stereochemistry)

MOISEYENKO, A.M.; AKHREM, A.A.

Analogs of corticosteroids. Report No.2: Different stability of
cis- and trans-1-acetyl-1,2-cyclohexanediol. Izv. AN SSSR. Otd.-
khim.nauk no.6:1064-1070 Je '63. (MIRA 16:7)

1. Institut organicheskoy khimii imeni N.D.Zelinskogo AN SSSR.
(Cyclohexanediol) (Corticosteroids)

PENTIN, Yu.A.; SHARIPOV, Z.; KOTOVA, G.G.; KAMERNITSKIY, A.V.; AKHREM, A.A.

Spectroscopic investigation of the conformation equilibrium of
chlorocyclohexane and bromocyclohexane. Zhur.strukt.khim. 4
no.2:194-200 Mr-Apr '63. (MIRA 16:5)

1. Moskovskiy gosudarstvennyy universitet imeni Lomonosova.
(Cyclohexane—Spectra)

UKHOVA, L.I.; AKHREM, A.A.; USKOVA, N.F.

Stereochemistry of the synthesis of
1,2-dimethyl-4-ethynyl-4-hydroxydecahydroquinolines. Izv. AN
SSSR Otd.khim.nauk no.5:951-953 My '63. (MIRA 16:8)

1. Institut fiziko-organicheskoy khimii AN BSSR i Institut
organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Quinoline) (Stereochemistry)

AKHREM, A.A.; KUZNETSOVA, A.I.

Thin layer chromatography. Usp. khim. 32 no.7:823-859
Jl '63. (MIRA 16:8)

1. Institut organicheskoy khimii AN SSSR imeni Zelinskogo.

MOISEYENKO, A.M.; AKHREM, A.A.

Analogues of corticosteroids. Report No.13: Cis-opening of
acetylcyclohexene oxide. Izv.AN SSSR.Ser.khim. no.8:1446-1451
Ag '63. (MIRA 16:9)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
(Corticosteroids) (Oxabicycloheptane)

AKHREM, A.A.; KOKHOMSKAYA, V.V.

Heterocyclic analogs of corticosteroids. Part 2: Syntheses
based on 2,2-dimethyl-4-tetrahydrothiopyrone. Izv. AN SSSR.
Ser. khim. no.12:2156-2165 D '63. (MIRA 17:1)

1. Institut fiziko-organicheskoy khimii AN BSSR i Institut
organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

AKHREM, A.A.; KAMERNITSKIY, A.V.; DUBROVSKIY, V.A.

Thermal isomerization in the 16 α , 17 α -dihydroxy 20-keto
steroid series. Izv. AN SSSR. Ser. khim. no.12:2237-2238
D '63. (MIRA 17:1)

1. Institut organicheskoy khimii AN SSSR im. Zelinskogo.

AKHREM, Afanasiy Alekseyevich; USTYNIUK, T. K.

"Rearrangement of 17-acetate-20, 21-dibromo- Δ^1 -pregnene-17 β -ol-3, 20-dione into isomeric Δ^1 -pregnene-17 β , 20 β -diol-21oic acids."

Report presented for the 3rd Intl. Symposium on the Chemistry of Natural Products (IUPAC), Kyoto, Japan, 12-18 April 1964

AKHREM, Afanasiy Alekseyevich; DUBROVSKIY, V. A.; KAMERNITSKIY, A. V.

"Thermal isomerization in the series of 16_a,17_a-dihydroxy-20-keto steroids."

Report presented for the 3rd Intl. Symposium on the Chemistry of Natural Products (IUPAC), Kyoto, Japan, 12-18 April 1964.

DUBROVSKIY, V.A.; AKHREM, A.A.; KAMERNITSKIY, A.V.

Transformed steroids. Report No.4: Synthesis, properties and transformations of 3β , 16α , 17α -trihydroxy- Δ^5 -pregnen-20-one. (MIRA 17:4)
Izv.AN SSSR. Ser.khim. no.1:103-111 Ja '64.

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.

PROKHODA, A.M.; KAMERNITSKIY, A.V.; AKHREM, A.A.

Stereochemistry of the reactions of nucleophilic addition to a carbonyl group. Report No.6: Reactions of 3-tert-butylcyclohexanone. Izv. AN SSSR. Ser. khim. no.6:1060-1068 Je '64.
(MIRA 17:11)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

AKHREM, A.A.; TITOV, Yu.A.; KRAVCHENKO, Z.A.

New synthesis of an analog of steroid compounds without the
ring B. Izv. AN SSSR Ser. khim. no.7:1355 J1 '64.
(MIRA 17:8)

1. Institut organicheskoy khimii imeni Zelinskogo AN SSSR.

AKHREM, A.A.; TITOV, Yu.A.; LEVINA, I.S.

Synthesis of 1-carbomethoxy-2-methyl-3-acetyl-4-(p-anisyl)-
 Δ^5 -cyclohexene. Izv. AN SSSR. Ser. khim. no.10:1911-1912
O '64. (MIRA 17:12)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

AKHREM, A.A. doktor khim. nauk

Symposium on the chemistry of natural compounds in Japan. Vest.
AN SSSR 34 no.11:99 N '64. (MIRA 17:12)

AKHREM, A.A.; TITOV, Yu.A.; LEVINA, I.S.

Synthesis of 2-methyl-3-ethyl-4(p-anisyl)- Δ^3 -cyclohexene-
1-carboxylic acid. Izv. AN SSSR Ser. khim. no.12:2246 D'64
(MIRA 18:1)

1. Institut organicheskoy khimii imeni N.D. Zelinskogo AN SSSR.

AKHREM, A.A.; OSETSIMSKIY, I.V.

Transformed steroids. Report No. 3: Reaction of hypobromous acid with
17-ethinyl- Δ^5 -androstene-3 β , 17 β -diol, diacetate. Izv. AN SSSR. Ser.
khim. no. 9: 1634-1640 S '64. (MIRA 17:10)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

AKHREM, A.A.; KAMERNITSKIY, A.V.; DUBROVSKIY, V.A.; MOISEYENKOV, A.M.

Mechanism of cis-opening of α -ketoxides. Izv. AN SSSR. Ser. khim. no. 9:
1726-1727 S '64. (MIRA 17:10)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

RESHETOVA, I.G.; AKHREM, A.A.

Transformed steroids. Report N.5: Cleavage of 5,6- and
20,21-oxides of steroids by fluorine-containing agents.
Izv. AN SSSR Ser. khim. no.1:79-88 '65.

(MIRA 18:2)

1. Institut organ. cheskoy khimii im. N.D. Zelinskogo AN SSSR.

AKHREM, A.A.; RESHETOVA, I.G.

Synthesis of 17α -ethyl- $5\beta,6\beta$ -epoxyandrosterane- $3\beta,17\beta$ -diol
from 3,5di- and 3,5,6-triacetates of androsterane- $3\beta,5\alpha,6\beta$ -
triol-17-one. Izv. AN SSSR Ser. khim. no.1:172-175 '65.
(MIRA 18:2)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

AKHREM, A.A.; KAMERNITSKIY, A.V.; DUBROVSKIY, V.A.; MOISEYENKOV, A.M.

One-stage synthesis of cis-diols from α -keto oxides. Izv. AN SSSR
Ser. khim. no.1:202-203 '65. (MIRA 18:2)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

AKHREM, A.A.; DUBROVSKIY, V.A.; KAMERNITSKIY, A.V.; MOISEYENKOV, A.M.

New single-stage way of synthesizing steroid cis-16 α , 17 α -diols
from keto oxides. Dokl. AN SSSR 162 no.4:811-813 Je '65. (MIRA 18:5)

1. Institut organicheskoy khimii im. N.D.Zelinskogo AN SSSR.
Submitted November 16, 1964.

FROKHODA, A.M.; AKHREM, A.A.; KAMERNITSKIY, A.V.

Stereocemical course of nucleophilic addition to the carbonyl group of cyclohexanes as dependent on the presence and orientation of polar substituents. Izv. AN SSSR. Ser. khim. no.9:1713-1714 '65. (MIRA 18:9)

1. Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR.

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APPROVED FOR RELEASE: 06/05/2000

CIA-RDP86-00513R000100620004-8"

Akhrem, I. S.

62-11-12/29

AUTHORS: Kursanov, D.N., Vol'pin, M. Ye.,
Akhrem, I. S., Kachkurova, I. Ya.

TITLE: Curtius' (Kurtsius) Rearrangement in the Series of Isomeric
Cycloheptatrienecarbonic and Norcaradienecarbonic Acids
(Peregruppirovka Kurtsiusa v ryadu izomernykh
tsiklogeptatriyenkarbonovykh i norkaradiyenkarbonovoy
kislot).

PERIODICAL: Izvestiya AN SSSR, Otdelenie Khimicheskikh Nauk, 1957,
Nr 11, pp. 1371-1378 (USSR)

ABSTRACT: Here Curtius' rearrangement in the series of isomeric α -
cycloheptatrienecarbonic-(I), (R = COOH), β -cyclohepta-
trienecarbonic-(II) (R = COOH), γ -cycloheptatrienecarbonic
-(III) (R = COOH) acids are systematically investigated.
It is shown that the rearrangement takes place under the
conditions here existing without an isomerization of the
migrating hydrocarbon radical.
For the first time here 1,3,5-, 1,3,6- and 2,4,6- cyclo-
heptatrienylisocyanate, norcaradienylisocyanate, 1,3,5-,
1,3,6, and 2,4,6-cycloheptatrienylurea, norcaradienylurea,
N-phenyl-N'-1,3,5-, 1,3,6- and 2,4,6-cycloheptatrienylurea

Card 1/2

AKHREM, I.S.

62-12-20/20

AUTHORS: Vol'pin, M.Ye., Akhrem, I.S., Kursanov, D.N.
 TITLE: Letters to the Editor (Pis'ma redaktoru)
 New Reactions of Tropyl Salts (Novyye reaktsii soley tropiliya).
 PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1957, Nr 12,
 pp. 1501-1502 (USSR)

ABSTRACT: It was shown that the salts of cycloheptatrienyl very easily alkylate the compounds with mobile hydrogen. Tropyl salts react with the same ease with various aliphatic aldehydes. Aliphatic and aromatic ketones when heated also enter into reaction with the salts of tropyl. The latter easily alkylates numerous aromatic compounds. Propyl differs from the other simple esters by the fact that it alkylates the esters of β -keto acids, β -diketones, and β -dicarboxylic acids easily in the case of soft conditions. Thus, cycloheptatrienylacetone acid ester is formed with aceto acid ester. The tropyl salts easily attach themselves to the compounds with activated short bonds (like vinyl esters, cyclopentadiene, phenyl acetylene, and others). The reactions investigated offer new possibilities for the synthesis of the derivatives of cycloheptatriene and tropyl. There are 4 references, 3 of which are Slavic.

Card 1/2

Letters to the Editor. New Reactions of Tropyli Salts

62-12-20/20

ASSOCIATION: Institute for Elemental-organic Compounds AS USSR (Institut
elementoorganicheskikh soedineniy Akademii nauk SSSR).

SUBMITTED: October 9, 1957

AVAILABLE: Library of Congress

Card 2/2 1. Tropyli salts-Reactions

USCOMM-DC-54782

AKHREM I. S.

79-2-10/64

AUTHORS: Vol'pin, M. Ye., Akhrem, I. S., Kursanov, D. H.

TITLE: The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds (Vliyaniye nukleofil'nosti aniona na kharakter svyazi v soyedineniyakh tropiliya)

PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol. 28, Nr 2, pp. 330 - 333 (USSR)

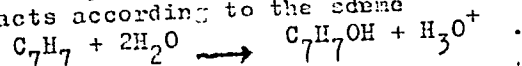
ABSTRACT: A number of salts of the aromatic 7-member cation of cycloheptatrienyl (tropilium) was recently produced (references 1 to 3). They are all salts of sufficiently strong acids ($X = Cl, Br, J, ClO_4, PtCl_6, B(C_6H_5)_4, HCO$). On the other hand the tropiliumoxide, methoxytropilium, tropilium cyanide, tropiliumthioether (references 1 and 2), where the X^- is an anion of sufficiently weak acids, are covalent compounds of type (II). Here and further the authors leave open the question whether the covalent tropilium derivatives possess a cycloheptatriene- or norcadiene structure (cf. reference 4). The authors made it their task to determine the boundary where the ionic compound $C_7H_7^+X^-$ transforms into the covalent compound C_7H_7-X . For this purpose they synthesized tropilium derivatives of acetic and benzoic acids ($K_a = 1.75 \cdot 10^{-5}$ and $6.3 \cdot 10^{-5}$). As well the tropilium acetate as the tropilium benzoate (more exactly the cycloheptatrienylacetate and -benzoate) proved to be typically covalent

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79-2-10/54

The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds

compounds - liquids - which can be solved in nonpolar solvents. Thus the transition from the ionic salts of tropilium to the covalent derivatives lies in the interval K_a of the corresponding acids. These results agree with the data by Dering (reference 1) that the tropilium ion behaves in water like the acid $K_a = 1.8 \cdot 10^{-5}$ and reacts according to the scheme



The results obtained point to the assumption that the acids with $K_a > 1.2 \cdot 10^{-4}$ will yield ionic salts with tropilium: the acids $K_a \leq 6.8 - 1.75 \cdot 10^{-5}$ must yield covalent compounds with tropilium. This result is confirmed by the results of the interaction of tropilium bromide or tropilium perchlorate and cyclopentadienylitium. The formation of the covalent compound is explained by the weak acid properties of cyclopentadiene and consequently by the considerable nucleophilia of the anion $C_5H_5^-$. The tropilium acetate and -benzoate were synthesized by means of acylation of tropilium oxide (dicycloheptatrienylether) with corresponding acetic and benzoic anhydrides. This method of ether production may have quite a general importance. The attempts to produce tropilium acetate by means of an exchange reaction of tropilium perchlorate and potassium

Card 2/4

75-2-10/5;

The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage in Tropilium Compounds

acetate in water and in alcohol were unsuccessful. Neither was it possible to produce tropilium benzoate by the exchange of potassium benzoate and tropilium perchlorate in water, nor by an exchange reaction of silver benzoate and tropilium bromine in alcohol or nitromethane. This indicates the instability of the cycloheptatrienyl ether and the inclination to hydrolysis. The covalent compound C_7H_7-X in tropilium cyanide and tropiliumcyclopentadienyl proved to be considerably stabler. It is interesting that in the acid process of the hydrolysis of tropilium cyanide a partial isomerization supposedly takes place and that phenylacetic acid is formed. Conclusions: 1) Tropilium acetate, -benzoate and cyclopentadienylcycloheptatriene which proved to be covalent compounds were produced. 2) It was shown that the nature of linkage of the cycloheptatrienyl residue with the anion depends on the nucleophilia of the anion. The transition from ionic to covalent tropilium derivatives lies in the range of K_a from $1.2 \cdot 10^{-4}$ to $6.3 - 1.75 \cdot 10^{-5}$. 3) It was shown that in the case of an acid hydrolysis of tropilium cyanide a regrouping with the formation of phenylacetic acid takes place. There are 6 references, 2 of which are Slavic.

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79-2-10/64
The Influence Exerted by the Nucleophilia of the Anion Upon the Nature of Linkage
in Tropilium Compounds

ASSOCIATION: Institute for Elemental-organic Compounds AS USSR
(Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

SUBMITTED: April 15, 1957

AVAILABLE: Library of Congress

Card 4/4

SOV/ 20-120-3-26/67

AUTHORS: Kursanov, D. N., Corresponding Member, Academy of Sciences,
USSR, Vol'pin, M. Ye., Akhrem, I. S.

TITLE: The Reaction of Tropylium Salts With Vinyl Ethers and Mercury
 β -Chloroacetaldehyde (Reaktsiya soley tropiliya s vinilovymi
efirami i β -khlormerkuratsetal'degidom)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 120, Nr 3, pp. 531-534
(USSR)

ABSTRACT: A characteristic property of the stable aromatic cation of
cycloheptatrienylium (tropylium) is represented by its ca-
pability to react with nucleophilic reagents. (Ref 1). It
was to be expected that the electrophilic property of the
tropylium cation is sufficient also for a reaction with more
weakly nucleophilic reagents, as vinyl ethers. This actual-
ly was the case, as the tropylium salts react with simple
vinyl ethers in aqueous or alcohol solutions even in the
cold under a self-heating. This high reactivity is a result
of the influence of the electron-donor ether group. Compounds
with isolated or conjugated double bindings, however, without

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SOV/2-120-5-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β -Chloro-acetaldehyde

activating substances (as, for example, methylcyclohexene, cycloheptatriene and others), or with electron accepting substituents (cinnamic acid, acrylic acid, acrylonitrile, chloroallyl and others) do not react with tropylium salts under identical conditions. In all cases the same product results independent of the nature of the anion of the initial salt of tropylium (whether bromide or perchlorate) and independent of the character of the alkyl in the vinylalkyl ethers: cycloheptatrienyl acetaldehyde. This reaction is analogous to that of the addition of mercury salts to vinyl ethers (Ref 2). Therefore it could be assumed that the mechanism of interaction of the tropylium salts with vinyl ethers includes an attack upon the double binding of the vinyl ether by the ion $C_7H_7^+$. At the same time, or subsequently, an action of one molecule of the solvent (water or alcohol) takes place. An acetal or a semi-acetal is probably the intermediate product of the reaction. The reaction velocity with the tropylium salts is markedly reduced at the transition from the simple vinyl ether to the vinyl acetate. This apparently is connected with a partial withdrawal of electrons by the $C=O$ group.

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SOY20-120-3-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β -Chloroacetaldehyde

Cycloheptatriene acetaldehyde was also obtained by a counter synthesis, that is to say by a reaction of the tropylium salts (bromide or perchlorate) with mercury β -chloroacetaldehyde. Because of an exchange of an Hg-atom with a tropylium radical an aldehyde was produced, which was identical with that produced from vinyl ethers. This is the first case to be investigated of an interaction of organomercury compounds with tropylium salts. The reaction of the tropylium salts with mercury β -chloroacetaldehyde proceeds according to the type of C-alkylation. The haloid acyls O-acylate mercury β -chloroacetaldehyde. There are 4 references, 3 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk
SSSR
(Institute of Elemental-organic Compounds AS USSR)

Card 3/4

SOV/20-120-3-26/67

The Reaction of Tropylium Salts With Vinyl Ethers and Mercury β -Chloro-acetaldehyde

SUBMITTED: January 14, 1958

1. Tropylium salts--Chemical reactions
2. Vinyl ethers--Chemical reactions
3. Mercury compounds (organic)--Chemical reactions

Card 4/4

AUTHORS: Zagorevskiy, V. A., Akhrem, I. S. SOV/79-29-2-56/7;

TITLE: On the Acylation of the Copper Acetoacetic Ester (Ob atsilirovanii med'atsetouksusnogo efira)

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 2, pp 619-624 (USSR)

ABSTRACT: Proceeding from the acylation of the copper acetoacetic ester the authors continued their investigation concerning the influence of the character of the acting reagent upon the direction of the substitution reaction at O or C. Acetyl fluoride, acetic acid anhydride and trichloro acetyl chloride were used as alkylating agents. The ever present marked inclination of silver derivatives of the keto enol system, as compared with the corresponding derivatives of alkali metals, to form O-substituted reaction products with alkyl halides and acyls (Refs 1, 2-4), is even more complicated in the case of copper enolates. Thus, the copper acetoacetic ester is acylated to the O-atom (Refs 5, 6) with acetyl chloride and benzoyl chloride, whereas the sodium acetoacetic ester chiefly forms C-derivatives. Apart from these examples no other indications concerning the acylation of copper derivatives of acetoacetic ester are available in publications. The authors found that acetyl fluoride, acetic

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On the Acylation of the Copper Acetoacetic Ester

SOV/79-29-2-56/71

acid anhydride and trichloro acetyl chloride react with the copper acetoacetic ester at the carbon atom (Table). On acylating with acetyl fluoride and acetic acid anhydride, the enolacetate of acetoacetic ester introduced on purpose into the reaction mixture is observed to reoccur unchanged with 78-90% (Table, Experiments 2,4,7). Consequently, it must be assumed that α -acetyl acetoacetic ester is a product of the primary substitution reaction and not of the secondary isomerization process of enolacetate. Since the reaction of sodium acetoacetic ester with acetyl fluoride or trichloroacetyl chloride is not described in publications, these reactions were carried out. Acetylfluoride yielded α -acetyl acetoacetic ester with sodium enolate (Table, Experiment 11). Acylation of sodium enolate with trichloro acetyl chloride led to ditrichloro acetyl acetoacetic ester (I) (40% yield), besides α -trichloro acetyl acetoacetic ester (II), which was identified on the basis of its copper derivative (III). The results obtained showed that the above three reagents behave towards copper acetoacetic ester in the same way as chlorocarbon and chloromethyl ester and sharply differ from acetyl chloride. There are 1 table and 19 references, 4 of which are Soviet.

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SOV/79-29-2-56/71

On the Acylation of the Copper Acetoacetic Ester

ASSOCIATION: Institut farmakologii i khimioterapii Akademii meditsinskikh nauk SSSR (Institute of Pharmacology and Chemotherapy of the Academy of Medical Sciences, USSR)

SUBMITTED: August 12, 1957

Card 3/3

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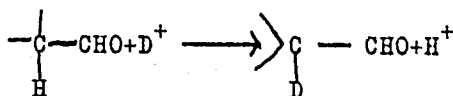
SOV/79-29-9-10/76

AUTHORS: Vol'pin, M. Ye, Akhrem, I. S., Kursanov, D. N.

TITLE: Reaction of Tropylium Salts With Aldehydes

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 9,
pp 2855 - 2857 (USSR)

ABSTRACT: The present paper deals with the investigation of the reaction of tropylium salts with aldehydes, basing on the papers quoted by references 1,2. Owing to the mobility of α -hydrogen atoms of aldehydes, hydrogen is readily replaced by deuterium or bromine in the latter (Ref 3). Various condensations are made possible thereby:

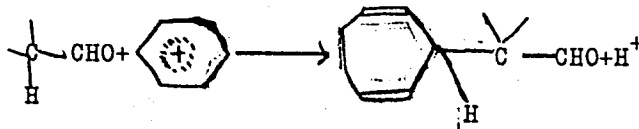


The authors found the cation of tropylium to react likewise with aldehydes. Already at room temperature (but more rapidly and in better yields at higher temperatures) one of the α -hydrogen atoms of aldehyde is replaced by the cycloheptatrienyl residue:

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Reaction of Tropylium Salts With Aldehydes

SOV/79-29-9-10/76



This course is followed by the reaction of tropylium bromide with acetic, propionic, isobutyric acid aldehyde, which contain three, two or one α -hydrogen atom, respectively. Mono-substituted aldehydes (I), (II), (III) were obtained in all cases. Tropylium salts react likewise with isovaleraldehyde and other aldehydes, whereas benzaldehyde, which has no α -hydrogen atoms, does not enter reaction with the above salts even not with longer heating. The structure of cycloheptatrienyl acetic and α -cycloheptatrienyl isobutyric acid aldehyde was proven by the identity with aldehydes forming in the addition of tropylium salts on the corresponding vinyl ethers (Ref 4) (Scheme 3). The frequency, typical of the carbonyl group, in the infrared spectra of the aldehydes obtained shows that there is no conjugation of the C=O group with the C=C double bonds occurring in them. Thus, tropylium salts

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